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# Electrodeposition of $TiO_2$ layer-by-layer assembled composite coating and silane treatment on Mg alloy for corrosion resistance

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## ABSTRACT

The layer-by-layer (LbL) assembly approach is a versatile way for the construction of multilayered nanoparticles coating. We demonstrated that the $TiO_2$ nanoparticles could be assembled on magnesium (Mg) alloys via the modification of opposite charged poly(styrenesulfonate) and polyethylenimine. Adsorption of the polyelectrolyte layer occurred in the beaker where particles and the selected polyelectrolyte solution were mixed, creating a layer of polyelectrolyte on the nanoparticles. Then these surfaced-modified nanoparticles were LbL assembled on the Mg alloy by electro-deposition. Finally, the surface silanization would prevent the peeling off of the $TiO_2$ nanoparticles and leads to stable assembly. The coated samples were examined using field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). The corrosion of the alloys was examined using potentiodynamic polarization, electrochemical impedance spectroscopy. The results show that a well-controlled and integrated silanized LbL system has been constructed via PMTMS and polyelectrolyte modified nanoparticles, which could provide good protection for Mg alloys.

## 1. Introduction

Magnesium (Mg) alloys have been intensively studied as biocompatible and biodegradable implant materials since they can corrode completely in physiological conditions which would eliminate the need for secondary surgeries for removal of implants [1–5]. However, the major drawback of Mg alloys is its poor corrosion resistance which limits the wider implantation of Mg as a biodegradable implant [6–8]. Thus, suitable surface treatments are necessary for the protection of Mg alloy.

The organosilanes have been successfully used to tailor metal material surfaces for preparation of hybrid materials by sol-gel processing [9, 10]. The sol-gel process generally includes hydrolysis and condensation of organosilanes. In the first process, the silanol alkoxy groups are capable of hydrolysis in the presence of moisture and form Si-OH. In the condensation process, the Si-OH groups could react with the metal hydroxide groups of the metallic substrate to form the Si-O-Me covalent bonded layer on the metal surface [11]. The Si-OH groups could also condense between themselves to form Si-O-Si chains. The silane films are chemically stable layers, therefore an effective barrier against chemical attack for the corrosion resistance properties is obtained [12–15].

We have constructed a polymethyltrimethoxysilane/micro-arc oxidation (PMTMS/MAO) composite coating to improve the corrosion resistance of the AZ31 substrate [16]. The MAO coating that is sealed with the PMTMS film acts as a physical barrier, effectively blocking the penetration of aggressive $Cl^-$ ions and $H_2O$ molecules. The self-healing of the PMTMS coating plays an important role in the long-term protection. While the coating thickness of the MAO coating is not easy to be controlled. It is significative to construct a composite coating with adjustable thickness based on the self-healing silane to satisfy the demand of different corrosion rate. Layer-by-layer assembled electrodeposition of nanoparticles may be a good way to obtain an adjustable three-dimensional (3D) structure.

$TiO_2$ nanoparticles are expected to highly improve the corrosion protective properties of the composite film [17]. It has been reported that some attempts have been made to use $TiO_2$ films as protective layers on the Mg alloys by sol-gel method and dip coating process [18, 19]. $TiO_2$ nanoparticles could also be added in the electrolyte to increase

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the corrosion resistance on the MAO coating of Mg alloys [20]. However, these results show that the corrosion resistance does not satisfy [21] or the overmuch $TiO_2$ nanoparticles would cause the damage of the coatings [20]. There could be degradation of $TiO_2$ particles or interfacial reaction at the particle-matrix interface [22]. What's more, nanostructured $TiO_2$/alginate composite coating also have been prepared on Mg alloy AZ91D via electrophoretic deposition, but the corrosion resistance of the composite coating is limited. To overcome these problems, silane film could be added as a matrix to produce a higher chemical stable composite coatings [23–25].

In addition, $TiO_2$ nanoparticles are featured by no toxicity, low cost and high stability in aqueous solution [26]. They have shown enhanced osteoblast cell proliferation on their surface in comparison with conventional (micrometric size) $TiO_2$, an improved cell response compared with other nanobiomaterials [27,28]. $TiO_2$ coating displays excellent bone-like apatite forming ability and can be anticipated as promising implant materials for orthopedic applications [29,30]. The silane modified $TiO_2$ nanoparticles might bring about additional functionalities such as biocompatibility and mechanical flexibility.

Furthermore, Ca—P coatings are of great interest in the application of biomaterials. Research has also proved the ability of Ca—P coatings in improving bone/tissue regeneration [31]. Most reported methods of obtaining Ca—P coatings on Mg alloys involve immersing the substrates in various types of SBF at different temperatures [32]. The polyelectrolyte may affect the rates and/or mechanisms of some or all of the main crystallization and aging processes of mineralization: nucleation, crystal growth, aggregation and phase transformation [33]. Our studies also presented that the polyelectrolytes easily lead to calcification in a solution of sodium ions [34,35]. Thus, the polyelectrolytes modified $TiO_2$ nanoparticles were chosen for this study due the expected advantages of their combined use.

In this work, a dense composite coating with polyelectrolytes modified $TiO_2$ nanoparticles as the inner layer and silane film as the top layer for the Mg-1Li-1Ca alloy was obtained. The degradation of the silane-$TiO_2$ coated alloy was evaluated by electrochemical measurement and hydrogen evolution test. The role of polyelectrolytes modified $TiO_2$ nanoparticles and silane on the corrosion behavior of the Mg alloy are presented and discussed. It is anticipated that the easily controllable composite coating could considerably increase the corrosion resistance of the Mg alloys and enhance our understanding about the direct deposition of the nanoparticles on the Mg alloys.

## 2. Experimental

### 2.1. Materials and chemicals

The substrate used was an novel as-extruded Mg alloy Mg-1Li-1Ca with nominal chemical composition (wt%): Li 1.26, Ca 0.95, and balanced Mg. poly(styrenesulfonate) (PSS, $C_8H_7NaO_3S$, MW = 70,000), polyethylenimine (PEI, $(C_2H_5N)_{14}$, MW = 600, 99.0%), and methyltrimethoxysilane (MTMS, $C_4H_{12}O_3Si$, MW = 136.22, 99%) were purchased from Qingdao Jingke Chemical Reagent Co, Ltd., China.

### 2.2. Alkaline treatment of the substrate

The substrates were cut into squares with dimensions of 20 mm × 20 mm × 5 mm and were ground with sand papers up to 1500 grit, then they were washed with a deionized (DI) water and alcohol solution and dried by warm air. The polished substrates were hydrothermal treated in a 1 M NaOH solution at 120 °C for 2 h, followed by thoroughly cleaning with DI water and dried at 120 °C for 1 h.

### 2.3. Preparation of coatings

Adsorption of the polyelectrolyte layer occurred in the beaker where 0.8 g $L^{-1}$ 25 nm together with 0.2 g $L^{-1}$ 100 nm $TiO_2$ particles were mixed up with the selected 0.3 g $L^{-1}$ PEI (pH 10) and 0.3 g $L^{-1}$ PSS (pH 10), respectively, creating a layer of polyelectrolyte on the nanoparticles via efficient stirring (PEI@$TiO_2$ and PSS@$TiO_2$). The $TiO_2$ coating were prepared using a electrodeposition method, performed on a direct-current power supply (QJ3010S) at a constant voltage for 10 min per layer at 60 °C. During electrodeposition, Mg plate was used as cathode to deposite first layer PEI@$TiO_2$ and parallel platinum plate as counterelectrode with a current of 0.2 A. After dried, depositing of second layer PSS@$TiO_2$, the above Mg plate was used as anode and parallel platinum plate as counterelectrode with a current of 0.3 A, then repeated for four times. The two electrodes were separated by a distance of 2 cm. Finally, the obtained samples were dipped in MTMS solution (MTMS: ethanol: DI water = 3: 10: 20) at 40 °C for 2 h. After heat treatment at 120 °C for 2 h, the PMTMS/$TiO_2$ coating were obtained. The preparation process was schematically illustrated in Fig. 1.

### 2.4. Surface analysis

The surface morphology of the coatings was investigated using field emission scanning electron microscopy (FE-SEM, Nova Nano SEM 450, Netherlands). The chemical bonding of the coatings was confirmed by means of fourier transform infrared spectroscopy (FTIR, Nicolet 380, Thermo electron, US) and X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo electron, US). The crystal structure of the samples was examined by X-ray diffraction (XRD, Rigaku D/MAX2500PC, Japan).

### 2.5. Corrosion testing

The electrochemical impedance spectra (EIS) and potentiodynamic polarization (PDP) were obtained using an electrochemical analyser (PAR Model 2273, Princeton, USA). A three-electrode cell set-up was used in which the prepared sample was the working electrode and a platinum sheet and a saturated calomel electrode were used as the counter and reference electrodes, respectively. The experiments were performed in Hank's balanced salt solution (HBSS: 8.0 g $L^{-1}$ NaCl, 0.4 g $L^{-1}$ KCl, 0.14 g $L^{-1}$ $CaCl_2$, 0.1 g $L^{-1}$ $MgCl_2 \cdot 6H_20$, 0.35 g $L^{-1}$ $NaHCO_3$, 1.0 g $L^{-1}$ $C_6H_6O_6$ (glucose), 0.06 g $L^{-1}$ $MgSO_4 \cdot 7H_2O$, 0.06 g $L^{-1}$ $KH_2PO_4$, 0.06 g $L^{-1}$ $Na_2HPO_4 \cdot 12H_2O$). A stable open-circuit potential (OCP) was established within 600 s prior to the EIS measurements. EIS studies were performed at a disturbing potential of 10 mV over a frequency range of 100 kHz to 0.01 Hz at OCP. Then, the polarization was performed from approximately −2000 to −1000 mV/SCE at a scan rate of 1 mV $s^{-1}$. The substrate, $TiO_2$ and PMTMS/$TiO_2$-coated substrates were prepared in quintuplicate for electrochemical testing. The repeatable results were chosen to be presented in Section 3.2.

The hydrogen evolution was recorded by placing the samples with full surfaces exposed into HBSS at 37 ± 0.5 °C under an inverted funnel connected to a graduated burette and measuring the solution level in the burette intermittently for 176 h [36]. Four parallel tests for hydrogen evolution were performed, the mean values and error bars of the hydrogen evolution rates (HERs) for all the samples were given.

### 2.6. Scratch testing

Scratch tests were carried out to characterize the coating adhesion (critical load) by MML Nanotest system (Micro Materials, Ltd). Scratches of length 2 mm were made using a diamond Rockwell indenter with a spherical tip radius of 25 μm sliding at a constant speed of 2 mm $min^{-1}$ under increasing loads from 0 to 10 N. The tests were repeated for three times. The scratch images were captured by using an in-situ optical microscope system in order to locate initial failure of the coating.